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## SURFACE OZONE VARIABILITY AT KISLOVODSK OBSERVATORY

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## ABSTRACT

The results of the surface ozone observations at the Observatory "Kislovodsk", situated in the North Caucasus at the altitude 2070 m a.s.l., are given. The observatory is in the background conditions and the variations of the surface ozone are determined by the natural dynamic and photochemical processes. The mean value of the concentration and its seasonal variations are very near to those obtained at the high-mountain stations in Alps (Reiter, 1987). The daily variations have the features, which remain stable during all warm period of the year (April-October). These features, including the minimum of the surface ozone at noon, are formed by the mountain-valley circulation. The significant variations of the surface ozone are connected with the unstationary lee waves.

## 1. INTRODUCTION

The long-term observations of ozone concentrations in the troposphere on the set of the ozonometric stations show that there is a positive trend of the troposphere ozone in the middle latitudes of the North hemisphere.

The tropospheric ozone has two sources: transport from the stratosphere and the photochemical generating in the polluted air. Their interaction determines the main features of the ozone behavior. It is difficult to divide their influence for the stations which are situated in the industrial area. Therefore the data got at the high-mountain stations are of the great value, as the local photochemical processes and any antropogenic factors play the insignificant role (Reiter, 1987). These data are the most informative for the analysis of the trends.

In April 1989 the regular measurements of the surface ozone concentrations at the "Kislovodsk"

Observatory were started. The Observatory is situated in the North Caucasus (43,7°N, 42,7°E, 2070 m a.s.l.) on the plateau in the zone of the alpine grasslands. The altitude of the plateau increases in the direction from N-E to S-W. The resort town Kislovodsk is situated 18 km away to the North. 48 km to the South there is the mountain Elbrus which together with the nearest mountain chains forms the local system of the air flows and is the source of the internal gravity waves. The prevailing air flow is of the western direction and is more strongly pronounced in winter. In summer and during the warming up in other seasons the active mountain-valley circulation is acting.

The Observatory is situated in clean background conditions. The only large source of the pollution in its environs is the town of Kislovodsk (800-870 m a.s.l.). Observations of nitrogen oxides (NO<sub>x</sub>) concentration with the help of the gas analyzer Antechnica AC-30 during 5 months in 1989 and 1990 gave their mean level below the level of the instrument's sensitivity which is 1ppb. In the present work the time variability of the surface ozone concentration in the mountains and the causes of these variations are analyzed.

## 2. OBSERVATIONS

The measurements of the ozone concentration were carried out with the help of the gas analyzer Dasibi 1008-AH which works on the base of the absorption of the UV-radiation. The precision of the measurements is about 1-2 ppb. The air was sampled on the level of 2,5 m above the ground.

The measurements are being carried out twenty-four-hour with the periodical switching off for the preventive inspection and because of the unfavorable meteo conditions: the intensive precipitations or the dense fog.

The ozone profile nicely demonstrates a pronounced laminar structure in the lower stratosphere, a recently much discussed phenomenon /5/.

Due to the fast response time, the ozone profiles obtained in a tandem balloon flight with a Brewer-Mast ozone sensor display a better spatial resolution in comparison to the latter sensor /6/.

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The analogous instrument was used for measurements of the ozone concentration in the south part of the town of Kislovodsk. The measurements there were carried out less regularly mostly in the daytime.

Both instruments were calibrated with the help of the ozone generator and compared with each other. The correlation coefficient between the instruments output was 0,98. The mean differences of the absolute values was 1 ppb.

The main information about the mean characteristics of the time variation of the ozone concentration at the Kislovodsk observatory are given in Tabl.1.

Tabl. 1. Mean values of the ozone concentration (ppb) at the station Kislovodsk.

Month 1989- 1990	Monthly means	Daily means		Hourly means	
		max	min	max	min
Apr	43 ± 3	46	30	56	33
May	44 ± 4	49	35	55	32
Jun	46 ± 6	55	39	59	35
Jul	41 ± 6	53	31	60	24
Aug	47 ± 4	56	41	61	32
Sep	41 ± 5	52	30	59	22
Oct	36 ± 2	40	32	42	28
Nov	32 ± 4	36	24	42	20
Dec	34 ± 3	39	26	40	21
Jan	32 ± 3	41	21	46	24
Feb	38 ± 4	48	26	51	23
Mar	42 ± 5	52	33	63	30
Apr	42 ± 6	56	33	57	21
May	44 ± 4	52	35	64	29
Jun	41 ± 5	49	29	63	29
Jul	44 ± 7	55	20	65	20

The averaged over year (April 1989-March 1990) ozone concentration was 39.7 ppb. It is approximately coincides with the mean values 40-42 ppb, got obtained Reiter et al.(1987) at the high-mountain stations in FRG Wank Peak, 1780 m a.s.l. and Zugspitze Peak, 2964 m a.s.l. (48 N) and slightly less than got at the high-mountain stations of the Japan at 32 N and 41 N - (45-47 ppb) (Tsuruta et al., 1989).

Hourly means of the ozone concentration during the same period varied within the limits of 20-65 ppb. The concentration equal or more 60 ppb were registered in total for 33 ours (only 9 days). During the day the hourly means vary insignificantly: minimum variation is 1 ppb, maximum - 25 ppb. Monthly means varied from 32 to 47 ppb. In Fig.1 the decade means of the ozone concentration at the Kislovodsk observatory are shown. Their values and seasonal variations are very similar to the data, given by Reiter et al.(1987) for the high-mountain stations in the Alps. The time of the



Fig. 1. The decade mean surface ozone concentration at the Kislovodsk observatory.

year maximum (May-August) and minimum (December-January) practically coincide as well.

At the stations situated below 1000m such as Kislovodsk town, Hohenpeissenberg Garmich-Partenkirchen (Reiter et al.,1987; Volz et al., 1989) the absolute values of the ozone concentration (yearly means - 24-32 ppb) and their variations differ significantly from the given above. The influence of the atmospheric pollution is noticeable there already.

The daily variations of the ozone concentration at the Kislovodsk Observatory (Fig. 2) is characterized by the small variations and high stability of the characteristic features from month to month. In contrast to the plain stations the stable minimum of the ozone concentration is registered there at the near noon time. This minimum is more deep (4-5 ppb) in June-July and disappears only in winter. Monthly mean time of the minimum existence varies from 11hours (local time)in June to 13 hours in April and October. There can be two cause of such stable and characteristic daily variations of the ozone concentration. The first one is the action of the photochemical processes in conditions of the low content of the nitrogen oxides ( $NO_x$ ) in the surface layer. The second one supposes the action of the dynamic mechanisms - the transport of ozone by system of the mountain - valley circulation in presence of the positive altitude gradient of the ozone concentration.

To our opinion, the daily variations can be explained in that way. The decreasing of the ozone concentration after the sunrise begins just as the N and N-E flows which moves upward the slope are formed. After the meteorological data the reiteration of the winds of these directions before noon during the warm period of the year make up 65%. In average, in 1-2 hours the air from the region of the higher border of the planetary boundary layer comes to the

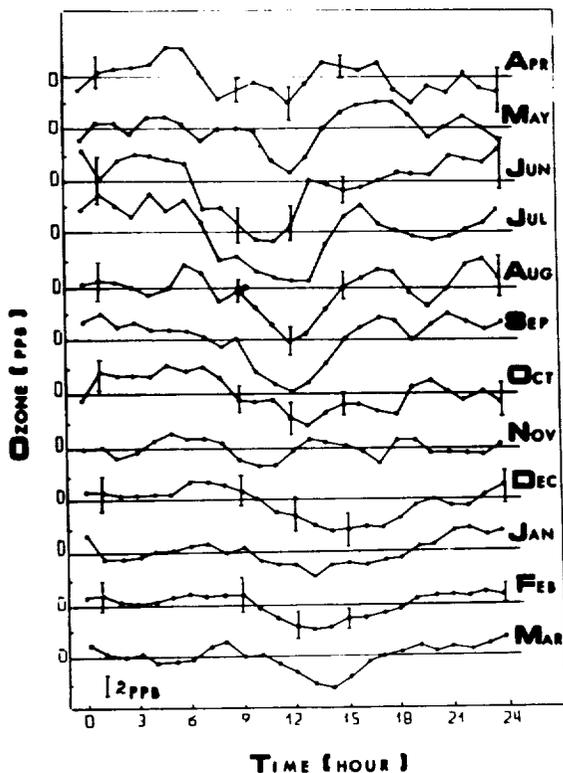


Fig. 2. Daily variations averaged by month for the period April 1989-March 1990.

observatory. This border is localized during the period from April to October at the mean altitude 1700 m. At all monthly mean diurnal profiles at this time the weak maximum of ozone is registered. The subsequent ascent of the air up the slope brings more poor by ozone but more polluted air from the valley and sometimes from Kislovodsk town. In this time the minimum of ozone is observed. When this air mass is rich with  $\text{NO}_x$  the intensive production of ozone under the influence of the sunlight is going on and the ozone concentration is increasing. This is demonstrated in Fig. 3. It is seen, that the daily variation of the ozone concentration at the Observatory got by averaging over the days when the direction of the wind was from Kislovodsk town is approximately the same as in the town after the noon. To the evening with the weakening of the photochemical processes the ozone concentration is decreasing but after the development of the downward flow is again increasing and stays on high level till the morning.

The unregular variations of the surface ozone are connected with the different meteorological processes: the

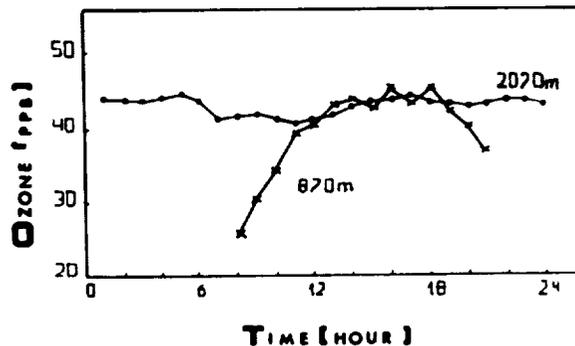


Fig. 3. The averaged over the period April-July 1989 (for the days with the North wind) daily variations of the ozone concentration at Kislovodsk town and the Kislovodsk observatory.

passing of the fronts, the intensive precipitations, fogs. In whole, the value and the character of such variations repeat the well known data for the plain stations. The characteristic features of the time variability of the ozone concentration at the observatory is the short-time (from 3 to 20 min) increasing up to 75-120 ppb and more. There was 6 such events in 1989. For these events the existence of the intensive jet streams in the upper troposphere the descending moving and internal gravity waves (IGW)

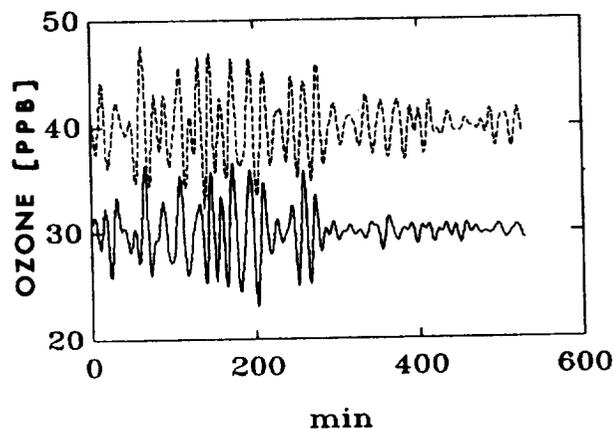


Fig. 4. The variations of the ozone concentration in 2 sites which are 250 m away from each other.

is characteristic . It says about the high probability of the descent of the stratospheric air in the zone of the tropopause break.

IGV of the orographic origin and from the developed convection play the significant role in the time variability of the surface ozone. The most characteristic periods of oscillations are 5-8; 12-16; 25-35 min. Unstationary waves reveal themselves in the observations in different sites. In Fig. 4 the example of such measurements carried out with the help of the chemoluminescent gasanalyzers in the points which are 250 m away from each other. The spectral analysis gives the periods of oscillations in each of these points 21 and 14 min and high values of coherency (0,8-0,9). The deviation of the phase of the oscillations corresponds to the time deviation 1-2 min. The vertical profile of the Brant-Vaisil frequency, got from the aerological data, says about the presence of the favorable conditions for the existing of the IGV with the periods 12-20 min in the layer 1.5-3 km.

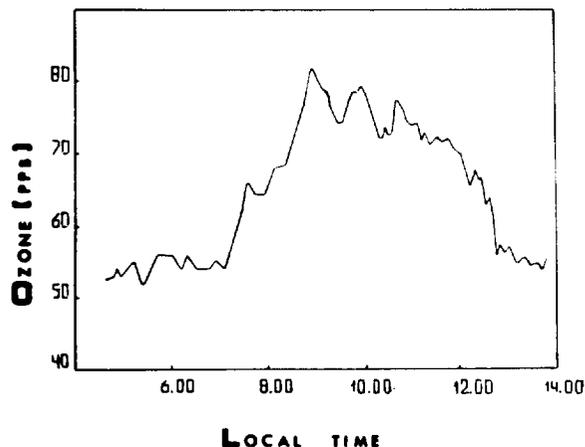


Fig. 5. The influence of the forest fire on the surface ozone concentration on 27 March 1991.

In Fig. 5 the great and prolonged increasing of the ozone concentration on 21 March 1991 is shown. It is connected with the violent forest fire 4-5 km away from the observatory. On this sunny day the concentration increased after the coming of smoke to the observatory and restored down to the normal level after the change of the wind direction.

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